

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE August 26, 1996 3. REPORT TYPE AND DATES COVERED Final Technical-Oct. 15, 1992/June 30, 199

4. TITLE AND SUBTITLE  
Superconductivity in Cage Doped Fullerenes

5. FUNDING NUMBERS

61103D  
3484/RS

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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AFOSR-TR-96

0467

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR /NE  
Department of the Air Force-AFOSR(AFMC)  
110 Duncan Avenue, Suite B115  
Bolling Air Force Base, DC 20332-0001

10. SPONSORING / MONITORING  
AGENCY REPORT NUMBER

F49620-93-1-0018

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Motivated by the discovery of superconductivity in alkali and alkaline earth fullerenes, this program was undertaken both to understand the nature of and expand the range of materials demonstrating superconductivity. The first approach involved attempts to modify the fullerene cage by incorporating heteroatoms in the structure and the preparation and photophysical properties of nitrogen and sulfur doped fullerenes were studied in detail. The second approach involved examining the stoichiometry and effect of preparative conditions on the behavior of alkali, alkaline-earth, lanthanide and mixed ion fullerenes. In particular, we have elaborated on a technique for making such salts using liquid ammonia or aliphatic amines as solvents. Thirdly, modeling studies were undertaken to predict the properties of heterohedral fullerenes and metal - C<sub>60</sub> complexes, and theoretical guidelines were developed for understanding the reactivity of the fullerene cage to common addition reagents.

14. SUBJECT TERMS

fullerenes, carbon 60, superconductivity, heteroatoms

DTIC QUALITY INSPECTED 2

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT  
unclassified

18. SECURITY CLASSIFICATION  
OF THIS PAGE  
unclassified

19. SECURITY CLASSIFICATION  
OF ABSTRACT  
unclassified

20. LIMITATION OF ABSTRACT  
SAR

## Introduction

Motivated by the discovery of superconductivity in alkali and alkaline earth fullerides, this program was undertaken both to understand the nature of and expand the range of materials demonstrating superconductivity. The first approach involved attempts to modify the fullerene cage by incorporating heteroatoms in the structure and the preparation and photophysical properties of nitrogen (s) and sulfur(s) doped fullerenes were studied in detail. The second approach involved examining the stoichiometry and effect of preparative conditions on the behavior of alkali, alkaline-earth, lanthanide and mixed ion fullerides. In particular, we have elaborated on a technique for making such salts using liquid ammonia or aliphatic amines as solvents. Thirdly, modeling studies were undertaken to predict the properties of heterohedral fullerenes and metal -  $C_{60}$  complexes, and theoretical guidelines were developed for understanding the reactivity of the fullerene cage to common addition reagents.

### I. Preparation And Photophysical Properties of N And S Doped Fullerenes

#### N-doped fullerenes

Samples of  $C_{60}$  and  $C_{70}$  containing a variety of nitrogen doped species were prepared by arc-vaporization of graphite in the presence of pyrrole. Cage doped fractions were isolated by column chromatography and also by high performance liquid chromatography using a gel permeation column. They were characterized by mass spectroscopy, optical absorption, fluorescence, transient absorption, and time-resolved fluorescence measurements. Mass spectra were consistent with the substitution of an even-number of carbon atoms of the  $C_{60}$  and  $C_{70}$  cages by nitrogen atoms. Carbonaceous clusters including fragmented fullerenes containing hydrogen atoms were also formed. UV-visible spectral analysis indicated that there is an influence of the molecular weight on the fundamental  $\pi$ - $\pi^*$  electronic transition. Fluorescence spectra showed a broad band containing vibrational fine structure that is attributed to photo-separated charges in the fragmented fullerenes and a shoulder on the low energy side that is related to intrinsic excitation in the nitrogen doped species. Fluorescence results imply a band gap of 2.36 eV for the N doped fullerenes and the existence of intermediate excitonic transitions below the optical band gap. Transient absorption spectra at time delays of 20 ns following excitation of the ground state molecules are attributed to

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delayed fluorescence. The average fluorescence lifetime of these molecules were determined to be 4 ns. Although it had not yet been possible to isolate a pure cage doped material, the photophysical studies added credence to their existence and the importance of further attempts at their isolation. Indeed, recently another group (F.Wudl et al., Science 269, 1554 (1995) ) has succeeded via insertion reactions into  $C_{60}$  to make small quantities of nitrogen doped fullerene dimers.

Details regarding these results are available in publications #5 and #6.

### S-doped fullerenes

Evidence was presented that carbon atoms of the hollow fullerene cage can be replaced by sulfur atoms, as has been suggested theoretically. S doped fullerenes were obtained by arc-vaporization of graphite in the presence of thiophene or 3-methylthiophene. Mass spectra indicated the dominant processes were the substitutions of pairs of carbon atoms by sulfur atoms with the predominant ratios of sulfur to replaced carbon pairs being 1, 1/3, or 1/4. Fractions which contained a large group of such compounds with a substantial S enrichment could be collected by column chromatography, but no single pure compound could be isolated. Since the mass spectra can be interpreted in alternate ways involving S incorporation as an adduct, evidence was sought for their existence from a detailed study of the fluorescence of these species. The fluorescence emission spectra were red-shifted from and consistent with absorption spectra, and can be attributed to the emission from symmetry-broken distorted S doped derivatives of fullerenes. An optical band gap of 2.5 eV was derived for the S doped fullerenes resulting from the splitting of the  $h_u$  degenerate state. The fluorescence lifetimes of these molecules were 2-7 ns, considerably larger than those of the undoped fullerenes.

These results were presented in detail in publication # 9.

## II. Intercalation of Alkali And Alkaline Earth Metals Into $C_{60}$ Using Monomethylamine And Liquid Ammonia as Solvent.

Several solid state and solution procedures had been developed to produce alkali and alkaline earth intercalated fullerene superconductors ( $M_xC_{60} M_{3-x}M'_xC_{60}$   $x = 3$ , where M, M' represent Na,

K, Rb, Cs). Among the solid state techniques which we have examined the most efficient were the direct reaction of stoichiometric amount of  $C_{60}$  with metal vapor and the method which uses  $M_6C_{60}$  as a starting material and then mixes an appropriate amount of  $C_{60}$  with it to obtain the desired stoichiometry. Solution techniques have also been developed using ammonia and monomethylamine as solvents to complement the solid state techniques.

The sample preparation techniques are briefly discussed below.

a. Solid state reaction: The  $M_xC_{60}$  samples with  $M=K$  and Rb were prepared by reacting weighed amounts of  $C_{60}$  and  $M$  in evacuated pyrex tubes. The  $C_{60}$  was first ground in an agate mortar in a glove box to enhance doping kinetics. Alkali metals were contained in 1-mm capillaries which were cut to length to give an approximate weight, which was then determined more accurately by subtracting the capillary weight using the known weight per unit length of an empty capillary. Batches of order 250 mg were prepared, resulting in an estimated error in  $M$  content  $x$  of  $\pm 0.01$ . An initial heat treatment at 250 C for 2 days sufficed to ensure that all the  $M$  was taken up by the  $C_{60}$ , after which the product was reground to ensure homogeneity, resealed and annealed for 5 days at higher temperatures.

b. Liquid ammonia solution: The binary  $M_3C_{60}$  samples with  $M=K$  and Rb and ternary  $M_xN_yC_{60}$  samples were prepared by dissolving the proper stoichiometric amounts of  $M$ ,  $N$  and  $C_{60}$  in liquid ammonia. About 10 ml of liquid ammonia was first condensed onto a dry ice/acetone cold finger (-78 C) and dripped into the reactor containing the solids. The reaction continued for 1 hour under a  $N_2$  atmosphere while the solution was stirred. The temperature was then raised to -55 C (dry ice/methanol) for another hour. The ammonia was evaporated and the powdery product was gently heated under dynamic vacuum at 90 C for 1 to several hours to remove any residual ammonia. Finally the samples were annealed at 150 C for 3 to 5 days.

c. Monomethylamine solution: The amine was first condensed into the first reactor containing the potassium. The potassium was allowed to react with the liquid monomethylamine until a permanent dark blue color appeared, characteristic of solvated electrons. The amine was then distilled over into the second reactor containing both the alkali metal and  $C_{60}$ . This second reactor was kept at -10 to -6 C for 1-3 hours. After the reaction was complete, the amine was allowed to boil off, leaving the solid intercalation compound on the reactor wall. The final products were sealed in quartz tubes, and annealed for 1 to several days.

Alkylamines and ammonia share the property of being solvents for both alkali metals as well as  $C_{60}$ , thus allowing one to obtain more homogeneous samples. The solution techniques are found to furnish an efficient method for producing a variety of intercalation compounds which typically have large superconducting volume fractions as well as the same  $T_c$  and lattice parameters achievable by the solid state techniques. We prepared several single phase stoichiometries like  $Rb_3C_{60}$ ,  $Rb_2CsC_{60}$ ,  $Rb_2KC_{60}$ ,  $K_2RbC_{60}$  and  $K_3C_{60}$  and we characterized them by x-ray diffraction and magnetization measurements. X-ray diffraction profile of  $Rb_3C_{60}$ ,  $Rb_2CsC_{60}$ , and  $K_3C_{60}$  were indexed on the basis of an face-centered-cubic unit cells with lattice parameters of 14.43, 14.45, and 14.24 Å, respectively, which are similar to those obtained in a solid state preparation. The temperature dependence of the dc magnetization of these samples display superconducting transition temperatures  $T_c$ = 29, 31, and 19 K respectively and very large superconducting fractions which are close to 100%. The high volume fraction of superconductivity observed in these compositions reflects the accuracy of the end-product stoichiometry.

#### Magnetization measurements

Magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer. Samples were cooled in zero field to 2K, a specific field was applied, and the zero field cooled (ZFC) data were taken as a function of increasing temperature up to  $T > T_c$ . The field cooled (FC) data was then measured by decreasing the temperature to 2K in the same field. The superconducting transition temperature was determined from the onset of diamagnetism of both the ZFC and FC curves. In the case of time decay of magnetization, the samples were first cooled in zero field to a desired temperature below  $T_c$  and then a magnetic field was turned on and the magnetization was measured as a function of time for up to 15 hours. After the measurements at a given temperature and field were completed the samples were heated up to 60K in order to remove the trapped magnetic flux lines.

Details regarding these results are available in publications #10 and #11.

#### III. Magnetic properties of superconducting fullerenes $M_3C_{60}$ with $M=K$ and $Rb$

The zero-field and field cooled magnetic susceptibility of  $M_3C_{60}$  with  $M=K$  and  $Rb$  exhibits irreversible behavior. The demarcation between reversible and irreversible behavior, the point at

which the ZFC and FC curves join which is denoted by  $T^*$ , represents the vortex-glass to vortex-fluid transition. We have reported that the experimental  $T^*$  data can be fit well to the de Almeida-Thouless relation  $H=H_0[1-T^*(H)/T^*(0)]^\gamma$ , where  $\gamma=3/2$  for both  $K_3C_{60}$  and  $Rb_3C_{60}$  compounds (publication #2). This behavior is similar to that found in the granular cuprate superconductors.

We have also measured the temperature and field dependence of the time decay of the magnetization for  $K_3C_{60}$  and  $Rb_3C_{60}$  (publication #3). For  $T \geq 6K$  an applied field of 2 KOe can fully penetrate the sample. At  $T=6K$  a linear logarithmic time decay behavior persists for the first several hours, and a very slight curvature appears for longer times. The deviation from linear curvature appears at earlier times for higher temperatures. At  $T=25K$  a nonlinear logarithmic time decay behavior occurs for the entire measurements. This nonlinear logarithmic time decay behavior can be explained by the collective creep model, i.e.  $M(t) \approx [\ln(t)]^{-1/\mu}$ .

#### IV. Magnetic properties of Yb doped fullerenes

Pure Yb metal shows a slightly enhanced Pauli magnetic susceptibility. We have prepared the  $Yb_xC_{60}$  compounds with  $0 < x \leq 6$  from liquid ammonia solution. The annealing temperature for these compounds was much higher than that for the alkali metal doped fullerenes. We have measured the temperature and magnetic field dependence of the magnetic susceptibility for these compounds. The results (unpublished) show a Curie-Weiss like behavior at low temperatures. The magnetic susceptibility at the lowest temperature measured here (2K) is greatly enhanced. This significant enhancement of magnetization is quite interesting, and further measurements to understand the mechanism of this behavior need to be undertaken.

#### V. Critical-field measurements; evaluation of coherence length and penetration depth of $Rb_2NaC_{60}$ .

Two temperature dependent characteristic lengths are critically important for characterizing the superconducting state of metal-doped  $C_{60}$ : the superconducting coherence length and the penetration depth. The coherence length  $\xi$  is a measure of the spatial extent of a superconducting pair and defines the distance over which superconductivity exists. The penetration length  $\lambda$  defines the distance over which a magnetic field will penetrate into a superconductor. The values of these two parameters can be used to calculate several intrinsic properties of the materials in their normal and superconducting state. These two parameters can be determined using the dc-magnetization



technique from the temperature dependence of the lower  $H_{C1}$  and upper  $H_{C2}$  critical fields.

When attempting to prepare  $Rb_2NaC_{60}$  from liquid ammonia, one obtains a phase separated material, consisting of the energetically more stable superconducting  $Rb_3C_{60}$  and nonsuperconducting  $Na_xC_{60}$ . This sample exhibits a well defined superconducting transition temperature at 26.3 K and a large volume fraction of 88%. Since  $Na_3C_{60}$  component of the sample does not superconduct, one can attribute the large fraction of superconductivity to  $Rb_3C_{60}$  being in particularly high purity in these samples. The decrease in  $T_c$  with respect to that of pure-phase  $Rb_3C_{60}$  is explained as the result of the decrease in density of states in Josephson-like junctions formed between the two phases. This composition displays a large volume fraction of superconductivity, and all measurements of superconducting parameters are extremely well defined, implying high phase purity of the  $Rb_3C_{60}$ . We have evaluated, the lower and upper critical fields of this composition. The temperature dependence of the lower critical field  $H_{c1}(T)$  is determined by the field dependence of magnetization at several temperatures, and the zero temperature  $H_{c1}$  value is about 62 Oe. The penetration depth for this sample is then calculated from  $H_{c1}(0)$  and is about 3400 Å. The higher critical field  $H_{c2}(T)$  is also determined from the temperature dependence of magnetization at different fields, and the zero temperature  $H_{c1}(0)$  value is estimated to be 16.5 T. The coherence length of 44 Å is then calculated from  $H_{c2}(0)$  and is much larger than those previously reported for  $K_3C_{60}$  and  $Rb_3C_{60}$ . The critical current density of the  $Rb_2NaC_{60}$  sample measured at 6 K is calculated from magnetization measurements and found to be  $J_c = 7 \times 10^6$  A/cm<sup>2</sup>. This relatively increased  $J_c$  value is related to the improved intrinsic properties in these samples.

Details regarding these results are available in publication #11

## VI. Magnetic properties of EDTTTF- $C_{60}$

We have prepared the EDTTF- $C_{60}$  charge transfer complex using from liquid ammonia solution. The temperature and magnetic field dependence of the magnetization has been investigated for this material, and the results (unpublished) show that this compound undergoes a magnetic phase transition to a soft ferromagnetic state at about 10K. More Interestingly, this material undergoes a second transition and becomes a spin glass state below 5K. The detailed x-ray diffraction measurements and further magnetization studies are necessary to understand this

fascinating compound.

## VII. Computational Analysis

### a) Metal-C<sub>60</sub> Complexes

Computational analysis of metal-fullerene interactions clearly described differences in exohedral metal complexation and suggested that transition metals encapsulated in endohedral fullerenes might interact with the interior surface of the fullerene cage. The focus of this work was to understand the bonding of metallic species to the outside of the C<sub>60</sub> cage, primarily, as an understanding of the metal exohedral coordination would assist synthetic chemists in building sophisticated metal-C<sub>60</sub> complexes. The interactions between the metal and the fullerene were analyzed in terms of electron transfer affects and covalent bonding interactions. In all cases, the stability of the cage was carefully monitored as metallic addenda were added. Three primary binding sites were analyzed, the interior and exterior  $\eta^2$  - sites in which the metal is bound over a five membered ring of the C<sub>60</sub>; the  $\eta^2$  site directly over the 5-6' bond site and the  $\eta^2$  -site directly over the 6-6' bond site. In most cases, the  $\eta^2$ , 6-6' site proved to be the best site for metal coordination. Back bonding between the metal and C<sub>60</sub> are maximized at this site for the earlier transition metals. This stabilizing interaction is a simple consequence of the orbital symmetry of the LUMO state(s) of C<sub>60</sub> and that of the metal d-states. Almost all metal-C<sub>60</sub> complexes show coordination across the 6-6" linkage. This suggest significant coordinate bonding between the metal and the fullerene. Stable complexes of C<sub>60</sub> and copper were not identified in this study and to date no such complexes have been prepared or isolated successfully.

The first metal-ligand complexes of C<sub>60</sub> were nicknamed bunnyballs, as the metal-ligand addenda produced a set of "bunny ears" attached to the fullerene cage. Analysis of these L<sub>2</sub>-(Ru, Os and Mn)-C<sub>60</sub> showed that ligand states of the addenda, initially unoccupied and non-bonding with respect to the fullerene, could effect significant changes in the frontier character of C<sub>60</sub>. These states being of lower energy than the HOMO state(s) of C<sub>60</sub> become populated through electron transfer from the populated frontier states of C<sub>60</sub>. The cage becomes more electron deficient, a greater electron affinity of the cage is anticipated. The effect is described as a self-doping effect in which the "valence" band population of C<sub>60</sub> is altered by complexation.

Details are available in publication #1.



## b) Heterohedral Fullerenes: Stability and Substitution

Smalley and coworkers clearly established the stability of boron substituted fullerenes with their mass spectral analysis of  $C_{59}B$ ,  $C_{59}B_2$ ,  $C_{56}B_4$  and  $C_{54}B_6$ . This work, performed early on in fullerene chemistry showed that cage substitution could be performed and thus motivated our comprehensive analysis of stability factors and substitution chemistry of nitrogen and boron fullerenes.

Our study utilized both molecular and quantum mechanical tools to analyze electronic factors and structural distortions induced by heteroatom substitution. Analysis of substitutional isomers showed interesting differences between boron and nitrogen substituted fullerenes. The results of these studies are summarized below:

1. Nitrogen substituted  $C_{60}$  complexes were significantly less stable than those of boron. Quantum chemical calculations of covalent bonding energy in the fullerene cluster showed that the stability of  $C_{59}B$  was only slightly less stable than  $C_{60}$  while  $C_{59}N$  was destabilized to a much higher degree. A comparison of data from the molecular mechanics study showed sizable distortion of the cage at the substitution site for both nitrogen and boron, however this distortion was not as great for boron. Similarly, the energies favored the boron substituted fullerene.
2. Cations of  $C_{59}N$  appeared to be more stable than the neutral species. A study of redox effects on  $C_{59}X$ , where  $X = B, N$  was performed to determine if the major contribution to the instability of the heterohedral fullerenes was simply due to orbital population effects. In the case of boron, the HOMO state are deficient by an electron with the substitution, while in the case of nitrogen the more antibonding LUMO states become populated. This study showed significant restoration of bond energy for the single reduced  $C_{59}B$  species,  $C_{56}B^-$ . Oxidation, of  $C_{59}N$  to the mono-cation similarly showed an increase in stability, though not as significant in the boron analog. A careful analysis of populated bonding states suggested that bonding states were destabilizing by the introduction of the more electronegative substituent as several bonding orbitals became more localized at the nitrogen site. Similar localization occurred for boron substitution, but this localization occurred in higher energy orbitals, some of which were not populated.
3. Dimers of heterohedral fullerenes may be stable. Molecular mechanics study suggested that

dimers of the singly substituted fullerenes would be stable. The dimers could form between  $C_{59}B$  and  $C_{59}N$ ,  $C_{59}N$  and  $C_{60}$ ,  $C_{60}$  and  $C_{59}B$  etc. Quantum chemical calculations showed similar trends in bond energies.

Recently, Labes and coworkers reported the synthesis of nitrogen substituted  $C_{60}$ . In his work he suggests that  $C_{59}N$ ,  $C_{53}N_2$ ,  $C_{56}N_4$ , could be prepared in significant quantities, though separation and isolation proved difficult. Their attempt at separation using chromatographic techniques led them to the conclusion that the nitrogen substituted fullerenes existed as dimers in solution. Wudl and coworkers more recently reported the synthesis of  $C_{59}N$  and suggested that it might exist as a cation. Our computational studies preceded these experimental works, therefore have proven to be somewhat predictive and have aided in the understanding of their data.

#### 4. Nitrogen and boron add across 6-6' and 5-6' bond types respectively.

Experimental work suggests that all heterohedral fullerenes are closed shell species, i.e., all nitrogen and boron substituents must add in pairs, that is except in the case of  $C_{59}N$  and  $C_{59}B$ . This observation suggested that substitution must be well defined and must occur in specific sites. In this study we considered multiple sites, the 5-6', 6-6' and sites in which all direct bonding interactions of the two substituents is eliminated. This analysis suggested that boron species would substitute in across the 5-6' bond while nitrogen species would substitute in the 6-6' site. This appeared to be a simple consequence of electronegativity affects. In fact, these two sites were the lowest of all sites considered.

Details are given in publication #7.

#### **c) Addition Chemistry of $C_{60}$**

The cage chemistry of fullerenes has expanded to a large number of additions, oxidations aminations etc. This component of our work was directed at understanding the mechanism of addition for halogens and nitrogen containing compounds. In the case of the halogens limited NMR data existed which suggested, 1-2, 1-3 or 1-4 isomers of difluoro- $C_{60}$  compounds were stable. 1-2, 1-3 and 1-4 refer to substitution sites within a single six membered ring of the  $C_{60}$ . Our mechanistic study was directed at answering the following questions:

- (1) Do halogens add molecularly or by free radical addition processes?
- (2) Does the first addition drive regio-specificity for the second addition?

Both questions were answered in our study on halogen addition. Our calculations showed that

fluorine addition occurred in a free radical process and that molecular addition could not occur for fluorine. An examination of the frontier orbital energies and consideration of electron transfer effects showed that electron transfer from  $C_{60}$  to  $F_2$  was energetically feasible and therefore, moderate electron transfer into the LUMO of  $F_2$  would lead to dissociation of  $F_2$  at a distance beyond the limit of covalent bonding to  $C_{60}$ . In fact, the HOMO of  $C_{60}$  has approximately the same energy as the LUMO of  $F_2$  in this model. For the other halogens, the situation is somewhat different. The LUMO states are significantly higher in energy and therefore these states cannot be easily populated. Molecular or free radical addition may occur for chlorine or bromine.

The disposition of the  $C_{60}X$  with regard to the second halogen addenda is an interesting problem. There are several models in the organic chemistry literature suggesting that ortho, meta or para substitution of halogens can be achieved for a variety of aromatic compounds. Mono-addition of either fluorine or bromine affects the frontier states similarly. The frontier orbitals of the  $C_{60}X$  show considerable delocalization of orbital character. There is a concentration of orbital density at the para and meta position, although to a lesser degree for meta, upon the single atom substitution while the 5-6' or & 6' site, e.g. the 1-2 sites are nearly noded. Thus the frontier chemistry suggests that initial substitution should be para directing for either F or Br. In the case of F, the extreme localization affects cluster stability and thus produces the least stable addition isomer.

While in the case of Br the fullerene cage is less destabilized with the para site favored. Our calculations suggest that the fluorine addition is energetically favored in the 1-2 site and favored to a lesser degree in the 1-4 and 1-3. Similarly NMR studies suggest that the all three species may be isolatable and that the 1-4 isomer is most readily formed. Here it appears as though the 1-2 isomer though thermodynamically favored is not the kinetically favored isomer, therefore it is likely that 1-4 and 1-3 isomers form initially and then isomerize to produce the 1-2 isomer.

The addition of  $NO_2$  and  $NH_2$  have been analyzed as well. In the case of amine addition, the 6-6' isomer appears to be the most stable. Here, the steric interaction of hydrogen is minimal and at this limit of interaction, population of the LUMO states of  $C_{60}$  appears minimal. Thus the C-N interaction can occur without significant loss of cluster stability. The situation for  $NO_2$  addition is somewhat different. Strong interaction occurs between the oxygen species of the nitro addenda and thus a more "rigid" structure is found by MM geometry optimization. In the case of the amine addenda, some rotation freedom is observed. For the nitro- addition, both 5-6' and 6-6' sites possess nearly the same

stability. In all cases, the antibonding LUMO states of  $C_{60}$  are involved in the addition process. This suggests that the bonding between carbon and nitrogen is quite and only minor perturbations are seen in carbon-carbon cluster bonding. The HOMO-LUMO gap traces the energy trends of the cluster as anticipated. Variances in the MM energies when compared to those obtained from EH are due to steric effects induced by rotation freedom. A complete dynamics minimization should prove interesting in defining the lowest energy structure for these materials.

Details are presented in publication #8.

### Papers Published

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#### Dissertations

Feng Chen, Ph.D. 1994

S. Cooke, Ph.D. 1996

Yang-Cheng Fann, Ph.D., 1992

Francesca Filler, M.A. 1996

Mary Landis, M.A. 1996

David Singh, Ph.D., 1992

Shu-Hsien Wang, Ph.D., 1995

These dissertations are available through University Microfilms and are abstracted in Dissertation Abstracts.

#### **Presentations at Conferences**

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